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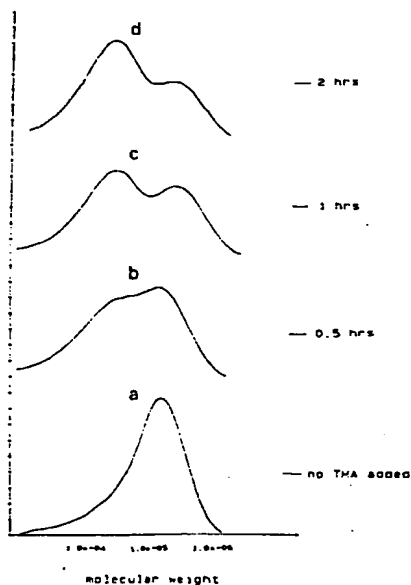
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⑤④ **Hafnium metallocene catalyst for the polymerization of olefins.**

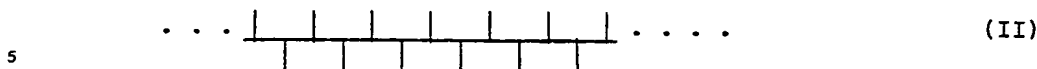
⑤⑦ The present invention provides a catalyst system for the polymerization and copolymerization of olefins with the system comprising a chiral, stereorigid hafnium metallocene catalyst in combination with an aluminum compound. The aluminum compound is preferably an alumoxane and may be a mixture of alumoxane and trimethyl aluminum. It was discovered that this mixture causes a transformation of the catalyst over time. The catalyst system may also include a solvent to increase the solubility of the metallocene catalyst. It was discovered that these catalyst systems produce useful polymer products with molecular weights greater than 10.000.

FIGURE

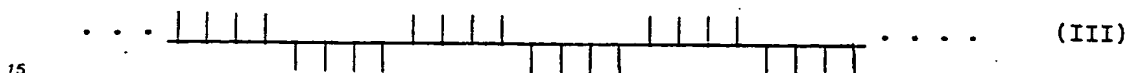


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by the structure



10 A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form. A polymer with recurring units of opposite configuration is an isotactic stereoblock polymer and is represented by



This latter type, the stereoblock polymer, has been successfully produced with metallocene catalysts as described in U.S. Patent No. 4,522,982.

20 A system for the production of isotactic polypropylene using a titanium or zirconium metallocene catalyst and an alumoxane cocatalyst is described in "Mechanisms of Stereochemical Control in Propylene Polymerization with Soluble Group 4B Metallocene/Methylalumoxane Catalysts," J. Am. Chem. Soc., Vol. 106, pp. 6355-64, 1984. The article shows that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl derivatives from isotactic polypropylene by the conventional structure predicted by an enantiomeric-site stereochemical control model. The meso achiral form of the ethylene-bridged
25 titanium indenyl diastereomers and achiral zirconocene derivatives, however, produce polypropylene with a purely atactic structure.

The above references generally describe metallocene catalysts as having two cyclopentadienyl rings attached to a transition metal. This general description would include a hafnium metallocene, but prior to the present invention, the references have disclosed only titanium and zirconium metallocene catalysts that
30 prove to be of any use. Heretofore, hafnium metallocene catalysts have not produced useful polypropylene products, in particular, as the molecular weights of the products have been well below 10,000. Hafnium could not simply be substituted for zirconium or titanium in known metallocene systems and produce useful results.

35 The present invention includes the discovery of a new type of hafnium metallocene catalyst not taught by the prior art. The catalyst exhibits properties and produces results that surpass those exhibited by zirconium and titanium metallocene catalysts with similar structures and used under similar conditions.

40 SUMMARY OF THE INVENTION

The present invention provides catalyst systems for the polymerization of olefins that include a chiral, stereorigid hafnium metallocene catalyst described by the formula $R^*(C_5(R')_4)_2HfQ_p$ and an aluminum compound; wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' is hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms, each R' may be the same or each may be different;
45 R^* is an organic or inorganic group providing a structural bridge between the two $(C_5(R')_4)$ rings imparting stereoridity to said catalysts; Q is a hydrocarbon radical such as an aryl, alkyl, alkenyl, alkylaryl or arylalkyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$.

Hafnium metallocene catalysts as described by the present invention are stereospecific and produce polymers with higher molecular weights than were previously known with metallocene catalysts. The
50 molecular weights are consistently above 10,000. These polymers are also highly stereoregular, have high crystalline melting points, and high optical activity. The catalysts of the present invention also show high efficiencies.

The hafnium metallocene catalysts of the present invention may also be used in the copolymerization of polyolefins, especially propylene and ethylene.

55 Also included in the present invention is the discovery of the effect of a mixture of alumoxane and trimethyl aluminum on a hafnium metallocene catalyst. A mixture of alumoxane and trimethyl aluminum causes a transformation of the catalyst over time. The transformed catalyst produces a polymer product with a low molecular weight and a relatively narrow distribution. The new catalyst retains, however, the

same degree of stereoregularity as the original form of the catalyst.

In another embodiment of the invention, a solvent is added to the catalyst system to increase the solubility of the catalyst in a solution of olefin(s). A preferred solvent is toluene, xylene or methylene chloride.

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DESCRIPTION OF THE FIGURE

The Figure shows the influence of trimethylaluminum on a hafnium metallocene of the formula $\text{Et}(\text{Ind})_2\text{HfCl}_2$, when used in combination with alumoxane. The Figure illustrates the formation of a bimodal distribution with time.

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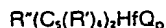
DETAILED DESCRIPTION

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The invention provides a hafnium metallocene catalyst system for the polymerization and copolymerization of olefins that provides a more useful product with higher molecular weights than was achievable with previously disclosed hafnium catalysts. The hafnium metallocenes also produce polymers that are more highly stereoregular and have higher molecular weights than the analogous zirconium metallocene catalysts. These and other beneficial advantages of the present invention will become more apparent from the following detailed description and accompanying examples.

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The hafnium catalyst of the present invention may be described by the following formula:



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wherein $(\text{C}_5(\text{R}')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl group; R' is hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms, each R' may be the same or different; R^* is an organic or inorganic group at least a portion of which acts as a bridge between the two $(\text{C}_5(\text{R}')_4)$ groups thereby making the catalyst stereorigid; Q is a hydrocarbon radical such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$. The catalyst should be chiral - i.e., non-superimposable on its mirror image --for the polymerization of propylene and higher alpha-olefins but need not be chiral or stereorigid for the polymerization of ethylene or predominantly ethylene copolymers.

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Exemplary hydrocarbyl radicals that may form a part of the catalyst as described above are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, methylene, ethylene, propylene and the like. Exemplary halogen atoms include chlorine, bromine and iodine with chlorine being preferred. Q is preferably a halogen and p is preferably 2. The R' substituents are preferably selected such that $(\text{C}_5(\text{R}')_4)$ forms an indenyl radical (Ind) which may be hydrated (IndH_4). As indicated, other hydrocarbon groups may be added to the cyclopentadienyl rings.

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R^* is a stable component that bridges the two $(\text{C}_5(\text{R}')_4)$ rings in order to render the catalyst stereorigid. R^* may be organic or inorganic and may include groups depending from the portion acting as a bridge. Examples of R^* include an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl group, a germanium hydrocarbyl group, an alkyl phosphine, an alkyl amine, boron, nitrogen, sulfur, phosphorous, aluminum or groups containing these elements. The preferred R^* components are methylene ($-\text{CH}_2-$), ethylene ($-\text{C}_2\text{H}_4-$), an alkyl silicon, and a cycloalkyl silicon such as cyclopropyl silicon, among others. The present invention is such that the R^* bridge and the R' substituents may be varied to provide polymer products with different properties.

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In the present invention, the hafnium metallocene catalysts just described are used in combination with an aluminum compound. Preferably, the aluminum compound is an alumoxane represented by the general formula $(\text{R}-\text{Al}-\text{O})$ for the cyclic form and $\text{R}(\text{R}-\text{Al}-\text{O})_n\text{AlR}_2$ for the linear form. In the general formula, R is an alkyl group with 1-5 carbons and n is an integer from 1 to about 20. Most preferably, R is a methyl group. Generally, in the preparation of alumoxanes from, for example, trimethyl aluminum and water, a mixture of the linear and cyclic compounds is obtained.

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The alumoxanes can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of trialkyl aluminum, such as, for example, trimethyl aluminum, in a suitable solvent such as benzene. Most preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate as described in U.S. Patent No. 4,404,344 the disclosure of which is hereby incorporated by reference. This method comprises treating a dilute solution of trimethyl aluminum in, for example, toluene with copper sulfate represented by the general formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The reaction is evidenced by the production of

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methane.

As part of the present invention, it was discovered that the use of a mixture of trimethyl aluminum and alumoxane in combination with a hafnium metallocene catalyst as described by the present invention caused a transformation of the catalyst. Alumoxane, containing only trace amounts of trimethyl aluminum (TMA), and the hafnocene catalyst produced a polymer product with fairly high molecular weights and that exhibited a fairly symmetrical distribution. (See Figure, curve a). The addition of about 1 mmol of TMA to 16 mmol of alumoxane caused a transformation of the catalyst over a period of 2 hours. A new catalyst was formed that produced a polymer with a lower molecular weight and a narrow distribution but with the same degree of stereoregularity as the original species. (Figure, curves "b-d"). As the polymerization proceeds for a longer period of time, the distributions increase at the lower molecular weight peak. This increase over time is shown in the Figure.

Also included in the present invention is the use of a solvent to increase the solubility of the catalyst in the monomer. In a preferred embodiment, the metallocene catalyst is used in a liquid form as is the olefin monomer. The solvent may be premixed with the catalyst or added with the monomer. The preferred solvents include toluene, xylene, and methylene chloride, but the solvent can be any organic solvent. As the catalysts usually are somewhat polar, it is preferred that the solvents exhibit some degree of polarity. Depending on the catalyst, a particular solvent may be more compatible with a particular catalyst than other solvents.

The hafnium metallocene catalysts of the present invention may be produced using any of the methods known to those skilled in the art. Typically, the procedures simply comprise the addition of an HfQ group as described above and a R' group to a starting compound such as indene or some other substituted dicyclopentadiene. An example of the production of the hafnium metallocenes as used in the Examples below is included in Example 1.

The polymerization procedures useful with the catalysts of the present invention include any procedures known in the art. An example of a preferred procedure would be that disclosed in copending application Serial No. 009,712, hereby incorporated by reference which describes a pre-polymerization of the catalyst before introducing the catalyst into a polymerization reaction zone. Another preferred procedure is illustrated in the Examples below.

The following Examples illustrate the present invention and its various advantages in more detail. Included with the Examples of hafnium catalysts are Comparative Examples using a zirconium metallocene catalyst to illustrate the increases in molecular weights and other polymer properties. The results are summarized in Table 1.

Example 1

Preparation of the Catalyst

A hafnium metallocene of the formula $\text{Et}(\text{Ind})_2\text{HfCl}_2$ was prepared by adding 38 mmol of n-butyllithium in hexane to a solution of 5 gm (19 mmol) of bisindenylethane in 150 ml of THF cooled to -91°C . The solution was warmed to 50°C , stirred for 3 hours, and then added dropwise to a HfCl_4/THF adduct solution (19 mmol in 150 ml of THF) at 150°C . After stirring overnight, the heat was removed and the solution was sparged for 15 seconds with HCl gas to produce a yellow solution. THF was roto-evaporated, and the solids were added to a small portion of CH_2Cl_2 . The solvent was decanted and the bright yellow solids were obtained by roto-evaporation and dried in vacuo. The yellow solids were dissolved in 100 cc of CH_2Cl_2 and the insoluble LiCl was filtered off. On addition of cold pentane, a few grams of bright yellow powder precipitated. The complex was filtered off, dried and further purified by fractional recrystallization from dry toluene at 0°C .

Polymerization of Propylene

(Polymerization Procedure No. 1)

In a 75 ml stainless steel sample cylinder filled with argon, a catalyst solution containing 0.14 mg of $\text{Et}(\text{Ind})_2\text{HfCl}_2$ and toluene was precontacted for 5 minutes with 10 ml of a solution of methylalumoxane in toluene. The contents of the sample cylinder were then injected by syringe into a 2 liter Zipperclave reactor

followed by the addition of 1.0 liter of propylene to the reactor at 50°C. The temperature was maintained at the reaction temperature of 50°C and the contents of the reactor were agitated for one hour. The propylene was then vented and the contents of the reactor were washed with 50% methanol in dilute HCl solution and dried in vacuo.

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Analysis of Polymer

The polymer product was then analyzed for the melting points and molecular weights. The melting points shown in Table 1 were derived from DSC (Differential Scanning Calorimetry) data as shown in the art. The melting points are not true equilibrium melting points but are DSC peak temperatures. True equilibrium melting points would be higher than the DSC peak melting points. The melting points for polypropylenes are determined by the crystallinity of the isotactic fraction of the polymer. The results showed only a difference of 1-2°C in the melting points after most of the atactic polymer was removed and isotactic polymer remained. This is shown to be true by running the DSC melting points before and after removal of the xylene solubles or atactic form of the polymer. The predominantly isotactic polymer yields a sharper and more distinct melting point peak.

The molecular weights of the polymers were calculated using GPC (Gel Permeation Chromatography) analysis. The analysis was done on a Waters 150 C instrument with a column of Jordi gel. The solvent was trichlorobenzene and the operating temperature was 140°C. The values for M_n and M_w and M_w/M_n are reported in Table 1.

Example 2

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The procedures of Example 1 were repeated except that 1.42 mg of catalyst was used and the reaction temperature was 80°C. The results are shown in Table 1.

Comparative Examples 3 and 4

The procedures of Example 1 were repeated except that a zirconium metallocene catalyst was used to compare the results obtained using the hafnium catalyst.

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Examples 5-7

The procedures of Example 1 were repeated except that the catalyst used was a hydrogenated form of the hafnium catalyst used in Example 1 with the structure $\text{Et}(\text{IndH}_4)_2\text{HfCl}_2$ and Polymerization Procedure No. 2 was followed. This procedure differs from that in Example 1 (Procedure No. 1) in that the propylene was added to the reactor prior to the addition of the catalyst/cocatalyst mixture. The reaction temperatures were varied as shown in Table 1.

Comparative Examples 8-10

These examples parallel those of Examples 5-7 using similar procedures but using a zirconium catalyst of the formula $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$. The results are shown in Table 1. Comparing the results in Table 1, the hafnium metallocene catalyst of the present invention produces polymer products that exhibit much higher molecular weights than the corresponding zirconium metallocenes under similar conditions.

Examples 11-16, 20

The catalyst preparation procedures of Example 1 were repeated for $\text{Et}(\text{Ind})_2\text{HfCl}_2$. Polymerization Procedure No. 3 was followed which is the same as Procedure No. 2 except that 500 ml of toluene and 800 ml. of propylene were added to the reactor and 200 ml of propylene were used to charge the catalyst/cocatalyst into the reactor. The other polymerization conditions were as listed in the Table.

TABLE 1

Example	Catalyst	Cat. mg	T _r °C	Poly. Procedure	Yield gms	Efficiency kg/g.cat. 1h	T _m °C	M _n /1000	M _w /1000	M _w /M _n
1	Et(Ind) ₂ HfCl ₂	0.14	50	1	2	13.9	134	64	273.0	4.2
2	Et(Ind) ₂ HfCl ₂	1.42	80	1	7	4.93	129	30	81	2.7
3	Et(Ind) ₂ ZrCl ₂	2.0	50	1	20	10.0	133	6.1	13.3	2.2
4	Et(Ind) ₂ ZrCl ₂	1.43	80	1	221	154.5	126	6.7	14	2.1
5	Et(IndH ₄) ₂ HfCl ₂	1.48	30	2	4	2.7	146	49	158	3.2
6	Et(IndH ₄) ₂ HfCl ₂	1.48	50	2	13	8.8	141	33	108	3.3
7	Et(IndH ₄) ₂ HfCl ₂	1.48	80	2	95	64.2	127	18	42	2.3
8	Et(IndH ₄) ₂ ZrCl ₂	19.6	20	1	17	0.8	143	9.7	28.0	2.9
9	Et(IndH ₄) ₂ ZrCl ₂	1.86	50	1	33	17.7	137	4.8	11	2.3
10	Et(IndH ₄) ₂ ZrCl ₂	3.38	80	1	265	78.4	121	3.2	5.6	1.8

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TABLE 1 (cont.)

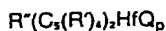
Example	Catalyst	Cat. mg	T _p ^o C	Poly. Procedure	Yield gms	Efficiency kg/g.cat. 1h	T _m ^o C	M _p /1000	M _w /1000	M _w /M _n
11	Et(Ind) ₂ HfCl ₂	0.17	50	3	9.0	53	136	193	724	3.8
12	Et(Ind) ₂ HfCl ₂	0.17	50	3	4.6	27	137	272	605	2.2
13	Et(Ind) ₂ HfCl ₂	0.17	50	3	6.4	37	138	170	442	2.6
14	Et(Ind) ₂ HfCl ₂	1.70	50	3	220.0	129	133	58	228	3.9
15	Et(Ind) ₂ HfCl ₂	1.70	50	3	80.3	47	134	111	310	2.8
16	Et(Ind) ₂ HfCl ₂	1.70	50	3	76.0	45	136	152	361	2.4
17	Et(Ind) ₂ HfCl ₂	3.40	50	4	230.0	68	134	130	304	2.3
18	Et(Ind) ₂ HfCl ₂	3.30	50	4	190.0	58	135	73	271	3.7
19	Et(Ind) ₂ HfCl ₂	3.40	60	4	120.0	35	133	73	248	3.4
20	Et(Ind) ₂ HfCl ₂	1.71	40	3	22.6	13	135	180	431	2.4

5 10 15 20 25 30 35 40 45 50 55

Claims

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1. A catalyst system for the polymerization of olefins and for the copolymerization of olefins comprising:
 (a) a chiral, stereorigid hafnium metallocene catalyst described by the formula



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wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; each R' is a hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms; R^* is an organic or inorganic group providing a structural bridge between the two $(C_5(R')_4)$ rings imparting stereo-rigidity to said catalyst; Q is a hydrocarbon radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$; and

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- (b) an aluminum compound.

2. The system of Claim 1 wherein $(C_5(R')_4)$ is selected from the group consisting of an indenyl radical and a hydrated indenyl radical.

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3. The system of Claim 1 wherein R^* is selected from the group consisting of: an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl group, a germanium hydrocarbyl group, an alkyl phosphine, an alkyl amine; boron, nitrogen, sulfur, phosphorous, aluminum and groups containing these elements.

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4. The system of Claim 1 wherein R^* includes an ethylene bridge.

5. The system of Claim 1 wherein Q is chlorine.

6. The system of Claim 1 wherein the aluminum compound is alumoxane or a mixture of alumoxane and trimethyl aluminum.

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7. The system of Claim 1 wherein the system produces a polymer with M_w greater than 10,000.

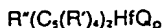
8. The system of Claim 1 further comprising (c) a solvent.

9. The system of Claim 8 wherein said solvent is selected from toluene, xylene and methylene chloride.

10. A catalyst system for the polymerization and copolymerization of olefins having three or more carbon atoms, said system comprising:

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- (a) a chiral, stereorigid hafnium metallocene catalyst described by the formula



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wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; each R' is a hydrogen or a hydrocarbyl radical having from 1 to 20 carbon atoms; R^* is an organic or inorganic group providing a structural bridge between the two $(C_5(R')_4)$ rings imparting stereo-rigidity to said catalyst; Q is a hydrocarbon radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$; and

- (b) an aluminum compound.

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11. The system of Claim 10 wherein $(C_5(R')_4)$ is selected from an indenyl radical and a hydrated indenyl radical.

12. The system of Claim 10 wherein R^* is selected from the group consisting of: an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl group, a germanium hydrocarbyl group, an alkyl phosphine, an alkyl amine; boron, nitrogen, sulfur, phosphorous, aluminum and groups containing these elements.

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13. The system of Claim 10 wherein R^* includes an ethylene bridge.

14. The system of Claim 10 wherein Q is chlorine.

15. The system of Claim 10 wherein the aluminum compound is alumoxane or a mixture of alumoxane and trimethyl aluminum.

16. The system of Claim 10 wherein the aluminum compound consists of about 0-20 mole percent of trimethyl aluminum and 80-100 mole percent of alumoxane.

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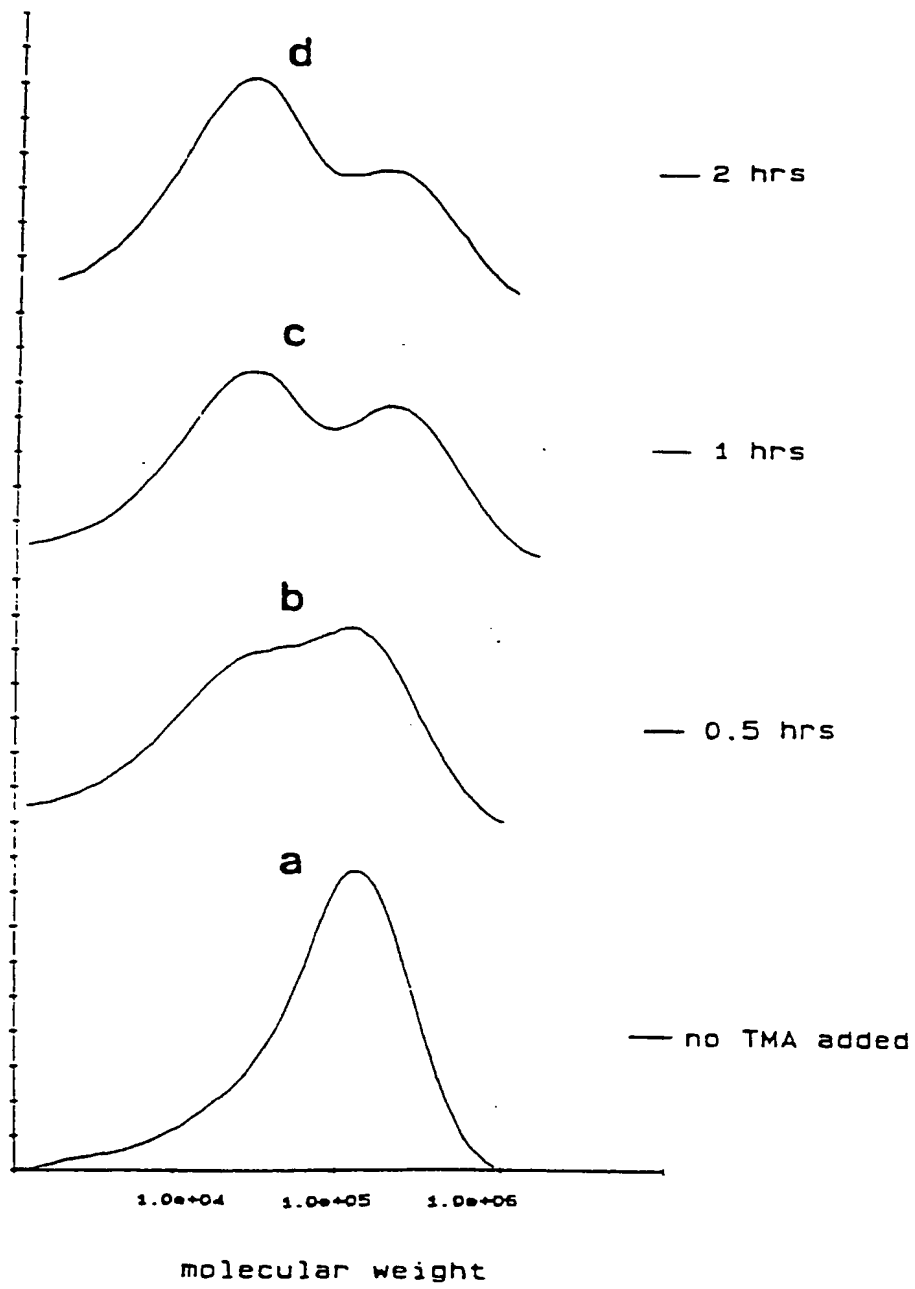
17. The system of Claim 16 wherein the system exhibits a transformation of the catalyst over time.

18. The system of Claim 17 wherein the transformation of the catalyst is characterized by the production of a lower molecular weight polymer product.

19. The system of Claim 10 further comprising (c) a solvent.

20. The system of Claim 20 wherein the solvent is selected from toluene, xylene, and methylene chloride.

FIGURE





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 129 368 (EXXON) * Claims; page 8, lines 23-24 * ---	1	C 08 F 4/64 C 08 F 10/00
A	DIE ANGEWANDTE MAKROMOLEKULARE CHEMIE, vol. 145/146, 1986, pages 149-160, Hüthig & Wepf Verlag, Basel, CH; W. KAMINSKY: "Stereoselektive Polymerisation von Olefinen mit homogenen, chiralen Ziegler-Natta-Katalysatoren" * Whole document * ---	1	
A	DIE MAKROMOLEKULARE CHEMIE/MACROMOLECULAR SYMPOSIA, vol. 3, June 1986, pages 377-387, Basel, CH; W. KAMINSKY et al.: "Olefinpolymerization with highly active soluble zirconium compounds using aluminoxane as cocatalyst" * Whole document * ---	1	
D,A	J. AM. CHEM. SOC., vol. 106, 1984, pages 6355-6364, American Chemical Society; J.A. EWEN: "Mechanisms of stereochemical control in propylene polymerizations with soluble group 4B metallocene/methylalumoxane catalysts" * Whole document * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) C 08 F
D,A	US-A-4 522 982 (J.A. EWEN) * Whole document * ---	1	
D,A	EP-A-0 185 918 (HOECHST) * Whole document * ---	1	
A	EP-A-0 197 319 (HOECHST) * Whole document * ---	1	
-/-			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-04-1988	Examiner DE ROECK R.G.
<p style="text-align: center;">CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p style="text-align: center;">T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	EP-A-0 128 046 (EXXON) * Claims 1,2 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-04-1988	Examiner DE ROECK R.G.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>----- & : member of the same patent family, corresponding document</p>			

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